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During the period of time, we purchased the new x-ray diffractometer and related hardware and installed this new instrumentation. The new equipment is working extremely well and has made a significant impact on our research effort. Our research focuses on the fabrication of nanolaminates with atomic layer deposition (ALD) techniques based on sequential self-limiting surface chemistry. We are also concentrating on measuring the properties of nanolaminates. Nanolaminates are multilayered thin film structures with very high interfacial density. These composite multilayer structures can display interesting properties that are not observed in the individual components. These special properties can be optimized by manipulating the thickness and composition of the individual nalolayers. The optimized nanolaminates may have important applications as better protective coatings and thin films with enhanced optical, mechanical and electrical properties.

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Final Report

"X-Ray Diffractometer for the Analysis of Structure and Thermal Stability of Nanolaminate Thin Films"

AFOSR Grant No. F49620-02-1-0195

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I. Overview

We received funding of $163,774 for an x-ray diffraction spectrometer under the Defense University Research Instrumentation Program (DURIP) for the Fiscal Year 2001. We were informed of this funding in April 2002. The funds were made available from May 1, 2002 to April 30, 2003. During this period of time, we purchased the new x-ray diffractometer and related hardware and installed this new instrumentation. The new equipment is working extremely well and has made a significant impact on our research effort.

Our research focuses on the fabrication of nanolaminates with atomic layer deposition (ALD) techniques based on sequential self-limiting surface chemistry. We are also concentrating on measuring the properties of nanolaminates. Nanolaminates are multilayered thin film structures with very high interfacial density. These composite multilayer structures can display interesting properties that are not observed in the individual components. These special properties can be optimized by manipulating the thickness and composition of the individual nanolayers. The optimized nanolaminates may have important applications as better protective coatings and thin films with enhanced optical, mechanical and electrical properties.

We needed the new x-ray diffractometer and related instrumentation to characterize the structure of our nanolaminates. Since the installation of the new equipment, we have used the new x-ray diffractometer extensively for x-ray diffraction (XRD) and x-ray reflectivity (XRR) measurements. XRD yields the crystal structure of the film. XRR yields the superlattice structure and also contains information about film density and interfacial roughness. The XRR measurements are critical to assess the nanolaminate superlattice structure.

II. Acquired Equipment

Using the funding provided by this DURIP grant, we obtained the following instrumentation:

1. Bede D1 High Resolution X-Ray Diffractometer

The Bede D1 High Resolution X-Ray Diffractometer was obtained from Bede Scientific in Englewood, Colorado. This x-ray diffractometer was selected after evaluating all available x-ray diffractometers for both XRD and XRR capabilities. The Bede D1 High Resolution X-Ray

Diffractometer produced the best results for XRR measurements. The Bede REFS4 software based on a genetic algorithm also was determined to produce the best fits to the XRR results for our nanolaminate superlattice samples. The total cost of this x-ray diffractometer was $162,900.

2. Haskris Model WW1 Non-Refrigerated Water-to-Water Recirculating System

After installation of the Bede D1 High Resolution X-Ray Diffractometer, we discovered that our process chilled water in the laboratory was too cold and water was condensing on the x-ray tube. This condensation problem required us to obtain a temperature-regulated water-to-water recirculating system. We obtained a temperature-regulated water-to-water recirculating system from Haskris. The total cost of this system was $2,572.00. We did not have sufficient funds to obtain this temperature-regulated water-to-water recirculating system entirely from our DURIP grant. Our parent AFOSR grant was used to provide the difference.

III. Research and Educational Use of Equipment

The new x-ray diffractometer for XRD and XRR have already greatly impacted our AFOSR-sponsored research and education. The new x-ray diffractometer was installed in October 2002. Since that time, the new x-ray diffractometer has been involved in much of our AFOSR-sponsored research on nanolaminates. The XRD capabilities have been invaluable to determine the crystal structure of our nanolaminates and other thin films. The XRR capabilities have been critical to assess the quality of our superlattice structures.

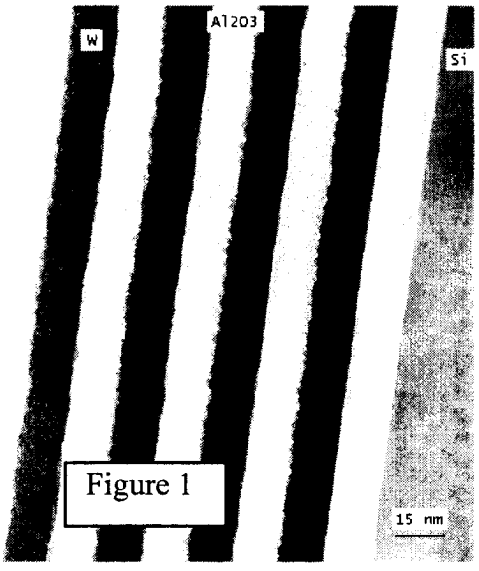

Figure 1

The highlight of our XRR measurements to date has been analysis of our W/Al_2O_3 nanolaminates. We have determined that these W/Al_2O_3 nanolaminates can display excellent x-ray reflectivity. Multilayer pairs of Al_2O_3/W nanolayers are deposited onto a silicon substrate using ALD techniques. The adjacent figure is a cross-sectional transmission electron microscope (TEM) image of the resulting structure. Alternating reflective layers (W, tungsten) and spacing layers (Al_2O_3,

alumina) are shown as deposited onto a silicon [Si(100)]. This superlattice is composed of four W/Al_2O_3 bilayers using the correct number of AB cycles to deposit individual W and Al_2O_3 layer thicknesses of approximately 125 Å. The alumina layers are the light regions and the tungsten layers are the dark regions in this TEM image.

The cross-sectional TEM image shows excellent reproducibility and conformality of the Al_2O_3 ALD layers and W ALD layers. The W/Al_2O_3 interface is extremely smooth in each instance because the Al_2O_3 ALD layers are amorphous and nearly atomically smooth. The Al_2O_3/W interface displays some greater roughness because the W layers are polycrystalline. However, the amorphous Al_2O_3 ALD on the underlying W layer results in some smoothing of this roughness.

X-ray reflectivity measurements of W/Al_2O_3 superlattices reveal the high quality of these multilayer samples. An example of the XRR measurements is shown in the adjacent figure. These x-ray measurements were performed on W/Al_2O_3 multilayers that contained 62 bilayer pairs and had a total film thickness of approximately 0.2 micrometers. The d-spacing for this multilayer was approximately 30 Angstroms. Each W and Al_2O_3 layer composing the bilayer had a thickness of approximately 15 Angstroms. These x-ray reflectivity measurements were performed with samples that were overfilled by the x-ray beam at close to grazing incidence. However, very pronounced Bragg peaks, or so-called "satellite" peaks were observed from the Al_2O_3/W multilayer. From the reflected x-ray intensity, the x-ray reflectivity was estimated to be in the range of 70-80% for the Cu Kα wavelength of λ =1.54 Angstrom used for the x-ray reflectivity measurements.

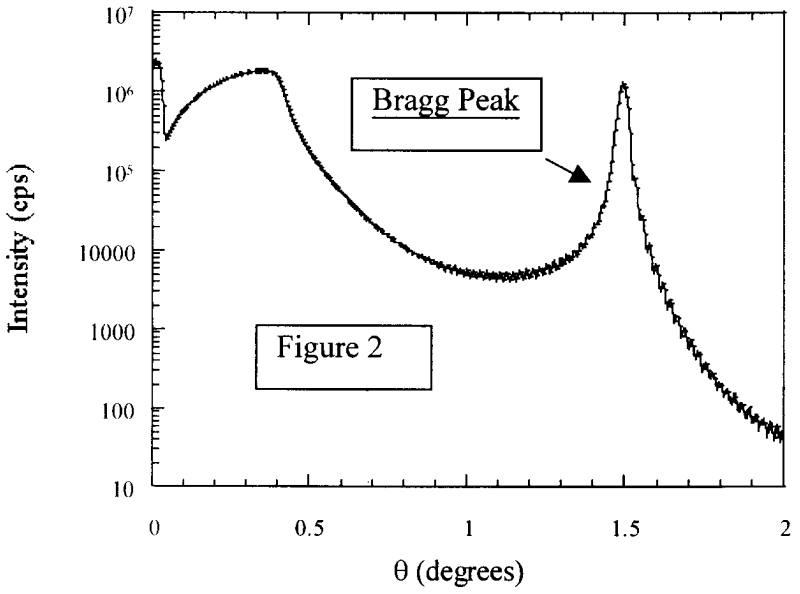

Figure 2

The high reflectivity in the hard x-ray region at λ =1.54 Angstrom is excellent and competitive with x-ray reflectivity from hard x-ray mirrors prepared using sputtering. The reflectivity is dependent upon a number of parameters that have not been optimized by the 62 bilayer W/Al_2O_3 multilayer. For example, the x-ray reflectivity is dependent upon the number of bilayers in the multilayer stack. Calculations indicate that x-ray reflectivity will increase further for up to 124 bilayers in the W/Al_2O_3 multilayer. In addition, the x-ray reflectivity will be dependent on the relative amount of W and Al_2O_3 in each bilayer. For convenience, the 62 bilayer W/Al_2O_3 multilayer was grown using equal thickness of W and Al_2O_3. Higher reflectivities are predicted for $W:Al_2O_3$ thickness ratios of 1:2 to 1:3.

Preliminary x-ray diffraction measurements of the W/Al_2O_3 multilayers are indicative of polycrystalline tungsten layers and amorphous alumina layers. The polycrystalline grains are consistent with α-W which has a body-centered cubic structure. The x-ray diffraction peaks are very broad as expected for extremely small polycrystalline grains. This polycrystalline structure is presumable responsible for the interfacial roughness on the W ALD nanolayers. This crystallinity could perhaps be suppressed by introducing an impurity into the W to prevent crystallization.

Besides the XRR and XRD measurements on our W/Al_2O_3 nanolaminates, we have also used the new x-ray diffractometer to examine other thin films. The new instrument has helped us characterize a variety of samples including Cu ALD films, hafnium oxide and hafnium silicate films, AlN films and Al_2O_3 films.

XRR is particularly valuable to determine film thickness and interfacial roughness of thin films. One of our recent studies examined Al_2O_3 ALD at low temperatures from 33 to 177°C using sequential exposures of $Al(CH_3)_3$ and H_2O. XRR results for Al_2O_3 ALD films grown using 300 $Al(CH_3)_3/H_2O$ reaction cycles are shown in Figure 3. The oscillations in the XRR intensity yields the film thickness and reveals

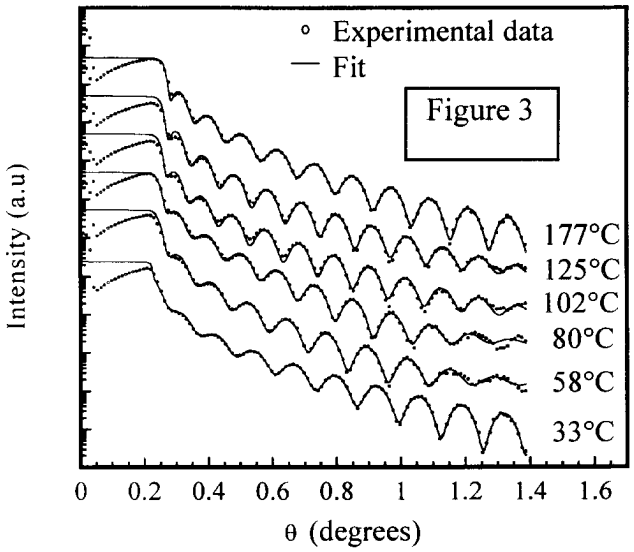

Figure 3

the low surface roughness and high optical quality of these Al_2O_3 films.

The new x-ray diffractometer has provided a superb educational experience for the undergraduates, graduate students and postdoctoral associates who have used the instrument. All the personnel have become acquainted with x-ray diffraction and x-ray reflectivity techniques. These valuable techniques are now becoming routine analysis tools for our nanolaminate and thin film research. The x-ray diffraction instrument has also exposed some of our limitations in determining the elemental composition of our films. Because we lack a compositional analysis tool such as depth-profiling x-ray photoelectron spectroscopy (XPS), we have resorted to using XRD for compositional analysis. We have recently submitted in a new DURIP proposal for a new depth-profiling XPS instrument that will complement our existing x-ray diffractometer.